



Electrochemical Potential Spectroscopy: A New Electrochemical Measurement

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$$(\partial\Delta H/\partial T)_P = nFT (\partial^2 E/\partial T^2)_P = \Delta C_P \quad [4]$$

and

$$(\partial\Delta S/\partial T)_P = nF(\partial^2 E/\partial T^2)_P = \Delta C_P/T \quad [5]$$

where ΔC_P is the change in heat capacity for a reaction at constant pressure. Since ΔC_P is relatively small for most reactions, both ΔH and ΔS are usually fairly constant over moderate temperature ranges, hence E vs. T will generally show a linear relationship as observed for the Li/SOCl₂ cell reaction. From heat capacity data,^{15,16,21} ΔC_P is only -4.2 cal/K for reaction [1] and -2.8 cal/K for reaction [2] per equivalent, hence ΔH^0 would change less than 0.5% over a 100°C temperature range for either reaction. Since $\ln K_{eq.} = -\Delta H^0/RT + \Delta S^0/R$, the constancy of ΔH^0 and ΔS^0 is also the basis of the linear relationship observed between $\ln K_{eq.}$ and $1/T$ for many reactions.²³

For the Li/SOCl₂ cell reaction below -20°C , another linear relationship between the open-circuit potential and the temperature is to be expected. Using $\Delta S = nF(\partial E/\partial T)_P$ and the data points at -40°C and -60°C in Fig. 6, it is found that $\Delta S = 58$ cal/K for a reaction involving one equivalent. At temperatures between $+72^\circ$ and -20°C , a quite different value of $\Delta S = 23.7$ cal/K is obtained. Any postulated changes in the cell reaction below -20°C should be consistent with abrupt changes in ΔH and ΔG to less negative values and with an abrupt increase in ΔS . Contrary to the statement by the authors (likely a misprint), ΔG is not constant over any temperature range for the Li/SOCl₂ reaction but varies directly with the cell potential according to $\Delta G = -nFE$.

Thermochemical calculations support the postulated formation of SO or (SO)_n. If about half of the sulfur-containing products in reaction [1] were actually present as SO, then the calculated value of ΔH^0 would be close to the experimental value of -77 kcal/eq. Differences reported between the experimental and standard state conditions would likely cause relatively small changes in the enthalpy for this cell reaction.

C. R. Schlaikjer:²⁴ The authors would like to thank Dr. Miles for submitting his comments.

For any electrochemical cell being discharged at vanishingly small current, the potential is determined by the free energy change associated with the electrochemical reactions occurring on the electrode surfaces. This potential is not affected by any chemical reactions involving products which may be present in the electrolyte subsequent to discharge, unless these products polarize one or both electrodes through direct chemical reaction. The enthalpy and entropy changes per equivalent for each of reactions [1] and [2], using the references cited by Dr. Miles, and those noted from the experimental data are as follows:

	ΔH^*	ΔS^{**}
reaction [1]	-86.1 kcal/eq. equiv.	-5.62 cal/deg equiv.
reaction [2]	-86.2 kcal/eq. equiv.	-9.78 cal/deg equiv.
found	-77 kcal/eq. equiv.	$+23.7$ cal/deg equiv.

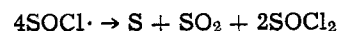
* Assuming SO₂ is formed as a condensed phase.

Apparently, neither reaction 1 nor 2 reflect the electrochemical reaction which occurs during the discharge of a Li/SOCl₂/C cell at ambient temperature, even though the over-all reaction may be as indicated in Eq. [1].

These observations and the arguments presented in the paper indicate that one or more intermediates exist in the solution as the result of discharge, which decompose on standing to sulfur and sulfur dioxide. The abrupt change in slope of the open-circuit potential as a function of temperature below -20°C may indicate that another discharge reaction becomes significant, but does not necessarily mean that the

electrode reactions produce Li₂SO₃ and sulfur directly. Dr. Miles used the two points at -40° and -60°C to calculate ΔS for the electrochemical reaction in this region. The observed dependence may be affected by the kinetics of the electrode reactions below -20°C . We believe that the data presented in the paper are not sufficient to establish what the slope $\partial E/\partial T$ really is in this region.

Blomgren *et al.*²⁵ have reported that the initial or electrochemical step in the reduction of both thionyl chloride and sulfur chloride involved the transfer of only one equivalent per mole. Dey *et al.*²⁶ also reported that solutions of thionyl chloride when reduced in supporting electrolyte did not yield two equivalents per mole, but fell short of this value by the time the SOCl₂ had disappeared. On standing, the electrolyte was said to have regenerated thionyl chloride, which on further electrochemical reduction yielded a total value near two equivalents per mole. If these observations are correct, then SOCl₂ could be an intermediate in the discharge of Li/SOCl₂/C cells



Dr. Miles mentioned a misprint on page 517, first column, 5th line from the bottom: the entry ΔG should read ΔH .

Electrochemical Potential Spectroscopy: A New Electrochemical Measurement

A. H. Thompson (pp. 608-616, Vol. 126, No. 4)

T. Jacobsen, K. West, and S. Atlung:²⁷ In the paper by Thompson the incremental capacity, defined as $-\Delta x/\Delta V$ is determined for Li_xTiS₂ by a potential stepping technique. The $-\Delta x/\Delta V$ vs. x dependence (Fig. 2 and 3 of the paper) shows definite peaks at $x = 1/9$ and $x = 1/4$. It is argued that due to the coulombic interactions superlattices of intercalated Li⁺ ions may be formed for $x = 1, 1/3, 1/4, 1/7, 1/9, \dots$ and the observed peaks are taken as a verification of the lattices $x = 1/9$ and $x = 1/4$.

Although we do agree with the author on the formation of regular structures during intercalation and his results are basically in agreement with our findings, we have some objections to his analysis of the capacity vs. composition dependence.

Consider the stage in the intercalation process, where a superlattice corresponding to $x = x_i$ has just been completed. On further intercalation this is gradually transformed into a new and denser lattice, which is completed at $x = x_{i+1}$. During this transformation all Li⁺ ions are inserted at position with identical nearest neighbor distances and to a first approximation the interaction energy of these ions will not depend on the degree of transformation. Later on when the $i + 1$ lattice is completed the Li⁺ ions now intercalated will have a shorter nearest neighbor distance and an increased interaction energy.

For $x_i < x < x_{i+1}$ the Li_xTiS₂ electrode potential can be written as

$$V = V_{0,i+1} + \frac{RT}{F} \ln \frac{1 - \theta_i}{\theta_i} + \Delta V_{int}(\theta_i) \quad [1]$$

where $V_{0,i+1}$ is the standard potential of the $i/i + 1$ lattice transformation. θ_i is the degree of transformation defined as $(x - x_i)/(x_{i+1} - x_i)$ and $\Delta V_{int}(\theta_i)$ accounts for the minor change in interaction energy during the transformation.

Ignoring the interaction term $\Delta V_{int}(\theta_i)$ the normalized differential capacity, $-dx/dV$, can be derived from Eq. [1]

²⁵ G. E. Blomgren, V. Z. Leger, M. L. Kronenberg, T. Kalnoki-Kis, and R. J. Brodd, Paper No. 36, "Power Sources 7," J. Thompson, Editor, p. 583, Proceedings of the 11th International Symposium, Brighton, 1978. Academic Press, London (1979).

²⁶ A. N. Dey, W. Bowden, J. Miller, and P. Witalis, Report DELET-TR-78-0563-1, April, 1979.

²⁷ Fysisk-Kemisk Institut, The Technical University of Denmark, DK 2800, Lyngby, Denmark.

²³ *ibid.*, pp. 170-173.

²⁴ GTE Laboratories, Waltham, Massachusetts 02154.

$$-\frac{dx}{dV} = \frac{-1}{x_{i+1} - x_i} \frac{d\theta_i}{dV} = \frac{F}{RT} \theta_i(1 - \theta_i) \quad [2]$$

As the term $\theta_i(1 - \theta_i)$ has a maximum for $\theta_i = 0.5$ this relation predicts capacity peaks to be present between the ordered structures. The differences in standard potential for the sequence of lattice transformations taking place during the complete discharge of Li_xTiS_2 is mainly determined by the decrease in nearest neighbor distance when denser structures are initiated. Therefore the capacity vs. composition relationship is expected to be a series of peaks, showing minimas where complete lattices are present. In case two (or more) lattice transformations have similar standard potentials the structure of intercalated Li^+ ions will be a mixture of the three (or more) lattices involved and the separating minimas may vanish.

Returning to Fig. 2 and 3 in Thompson's paper, it is seen that the capacity peaks at $x = 1/9$ and $x = 1/4$ are separated by a minimum for x close to $1/7$. Thus the first peak should preferably be attributed to the formation of the $1/7$ lattice. Although the expected minimum after the $x = 1/4$ peak is obscured by the superposition of denser structures, this peak is probably due to the transformation of the $1/7$ lattice into the $1/3$ lattice.

In a study of Li_xTiS_2 by means of slow linear potential sweeps we have obtained results very similar to the ones given by Thompson. At very slow scan rates, where the Li_xTiS_2 phase is close to equilibrium conditions, the observed current given by $i = Q_{\max} dx/dV dV/dt$ is proportional to the differential normalized capacity $-dx/dV$. Figure 1 shows this quantity determined at a sweep rate of $28 \mu\text{V sec}^{-1}$ as a function of the electrode potential. To analyze this we have assumed a series of consecutive lattice transformations each having an emf expression of the form

$$V = V_{0i/i+1} + \frac{RT}{F} \ln \frac{1 - \theta_i}{\theta_i} - f(\theta_i - 0.5) \quad [3]$$

where the interactions are accounted for by the term linear in θ_i . By differentiation it is easily seen that Eq. [3] predicts symmetrical peaks around $\theta_i = 0.5$

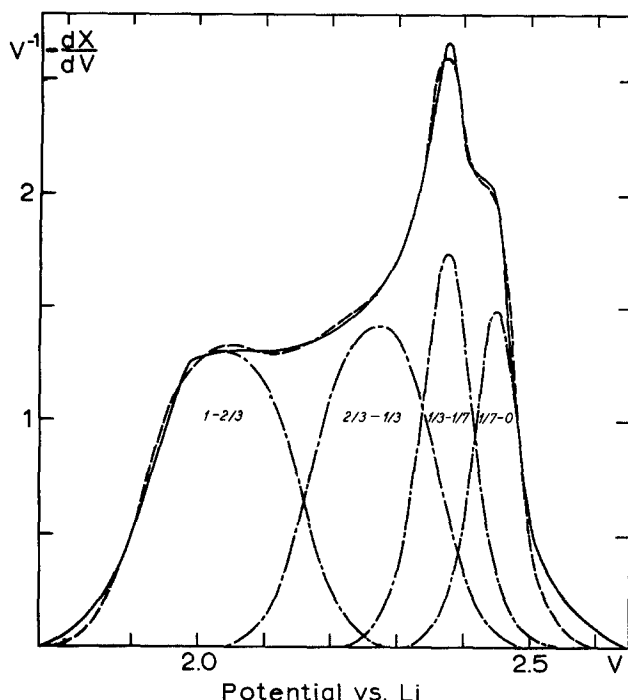


Fig. 1. Normalized differential capacity of Li_xTiS_2 vs. electrode potential determined by linear scan voltammetry (25°C , $28 \mu\text{V sec}^{-1}$): —, experimental; ----, calculated; - - - - -, contributions from the four lattice transformations considered.

Table I. Model parameters (Eq. [3])

Lattice	$V_{1/1+1}^0$ (V)	f (V)
0-1/7	2.455	-0.013
1/7-1/3	2.375	0.000
1/3-0.65	2.266	0.105
0.65-1	2.037	0.145

The peak width is determined by the interaction parameter f .

This model has been fitted to the experimental capacities by means of a nonlinear least squares computer program. The resulting calculated curve also given in Fig. 1 shows good agreement with the experimental one. As it is seen from the parameters in Table I the capacity behavior is described by the formation of a $1/7$ lattice, transformation of this into a $1/3$ lattice followed by a denser lattice at $x = 0.65$ before the complete close packed structure is formed. The value of $x = 0.65 \approx 2/3$ can be explained as a $1/3$ lattice of empty sites. The rather high values of the interaction parameter f for the dense states are not surprising as the Li^+-Li^+ distances in this region are small and interactions other than those between nearest neighbors may be of importance.

On the basis of these results the superlattice formation as suggested by Thompson appears a very suitable model for the intercalation of Li^+ into TiS_2 although more detailed studies are required to obtain a satisfactory description of the denser states.

A. H. Thompson:²⁸ The authors T. Jacobsen *et al.* raise some good points that were not fully discussed in my paper. I agree that the phase diagram for the Li_xTiS_2 system is still very much uncertain. The peaks in incremental capacity at the $x = 1/4$ and $1/9$ compositions seem to clearly suggest ordering effects. Also, the temperature dependent data clearly indicate that a probable ordering occurs at $x = 1/3$. But at present, there are not enough data to unambiguously specify the phase diagram. Additional electrochemical and particularly structural data are required. Nonetheless several specific replies need to be made to the Jacobsen discussion since I do not believe that the present data fully support the proposed model.

1. The model proposed by Jacobsen *et al.* assumes that all additional lithium ions intercalated between two ordered compositions enter identical sites. This would only be true if the ordered compositions are perfectly ordered and if the additional lithium do not interact with each other. The latter constraint would only be valid close to the x_1 composition. Also, the relatively high diffusivity of Li in Li_xTiS_2 suggests a highly defected structure involving both the octahedral and tetrahedral sites. Under these conditions, a highly defected or incipient model for the ordering is probably more appropriate.

2. The data of my paper do not support minima at $x = 1/7$ and $x = 1/3$. Close inspection of Fig. 3 shows that $x = 1/7$ lies on the falling edge of the $x = 1/9$ peak and that $x = 1/3$ lies on the falling edge of the $x = 1/4$ peak.

3. The qualitative differences between the electrochemical potential spectroscopy (ECPS) data and the linear potential sweep data may be explained by the rate differences. The ECPS data taken at $1-10 \mu\text{A/cm}^2$ correspond to continuous discharge rates of $10^{-2}-10^{-1} \mu\text{V/sec}$ compared to $\sim 30 \mu\text{V/sec}$ for the linear sweep data.

It should be further pointed out that minima in $-dx/dV$ would be expected when there is two phase formation. Recent studies on Li_xTaS_2 by the author^{29,30} describe ECPS results on two phase systems.

²⁸ Exxon Research and Engineering Company, Corporate Research Laboratories, Linden, New Jersey 07036.

²⁹ A. H. Thompson, To be published in the Conf. Proc., "Fast Ion Transport in Solids," Geneva, Wisconsin, May 1979.

³⁰ A. H. Thompson, *Physica*, To be published.